TABLE VII

THERMODYNAMIC PROPERTIES FOR ClF_3O

T, °K	$C_p°$, cal/mol	$H° - H_0°$, kcal/mol	$-(F° - H_0°)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	9.721	0.837	49.255	57.624
200	14.932	2.072	55.613	65.971
298.15	18.593	3.732	60.159	72.675
300	18.646	3.766	60.237	72.790
400	20.875	5.751	64.108	78.486
500	22.260	7.913	67.478	83.305
600	23.160	10.187	70.470	87.448
700	23.771	12.536	73.159	91.067
800	24.200	14.936	75.602	94.271
900	24.512	17.372	77.838	97.141
1000	24.744	19.835	79.900	99.736
1100	24.921	22.319	81.813	102.103
1200	25.059	24.818	83.595	104.277
1300	25.168	27.330	85.265	106.288
1400	25.256	29.851	86.834	108.156
1500	25.328	32.380	88.314	109.901
1600	25.387	34.916	89.715	111.538
1700	25.437	37.458	91.044	113.078
1800	25.479	40.003	92.309	114.533
1900	25.514	42.553	93.516	115.912
2000	25.545	45.106	94.668	117.221

the bands characteristic for ClF_2O^+[7] and ClF_4O^-[8] could be detected in the spectra of liquid or solid ClF_3O.

Thermodynamic Properties.—The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation.[28] These properties are given for the range 0–2000°K in Table VII.

Acknowledgment.—The authors wish to express their gratitude to Dr. D. Pilipovich for continuous encouragement of this work and stimulating discussions, and to Mr. R. D. Wilson for his help in the preparation of some of the samples. We are indebted to Dr. J. Cape of the Science Center of North American Rockwell Corporation for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Contract AF 49(638)-1734.

[28] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940.

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Chlorine Trifluoride Oxide. IV. Reaction Chemistry

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Reactions of chlorine trifluoride oxide, ClF_3O, with Cl_2, Cl_2O, $ClOSO_2F$, N_2F_4, HNF_2, and NF_2CFO are reported. In these reactions, ClF_3O either fluorinates, oxygenates, or both oxygenates and fluorinates the substrates. The interaction of ClF_3O with PtF_6 is also described. In this reaction, ClF_3O liberates F_2 and forms the new complex, $ClF_2O^+PtF_6^-$. Characterizing data for the complex are given.

Introduction

In the preceding papers,[1-3] we reported the preparation and properties of the new chlorine oxyfluoride, ClF_3O. Since ClF_3 is a powerful oxidative fluorinating agent, it was anticipated that ClF_3O would be similarly reactive as a fluorinating, as well as an oxygenating agent. This paper describes some of the reaction chemistry of ClF_3O.

Experimental Section

Apparatus.—Experimental techniques used in these studies were essentially the same as those described elsewhere.[1-4] Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (~0.5 mm o.d.). Gas chromatographic analyses were performed using the method of Dayan and Neale.[5] A Hanovia utility lamp (catalog no. 30620) was used for the photolyses.

Materials.—The preparation and purification of ClF_3O, Cl_2O, $ClOSO_2F$, HNF_2, and NF_2CFO are described elsewhere.[1,6-9] Chlorine (Matheson Co.), tetrafluorohydrazine (Allied Chemical Corp.), and platinum hexafluoride (Ozark Mahoning Co.) were purchased and purified by fractional condensations.

Reactions of Chlorine Trifluoride Oxide. With Chlorine.—At room temperature, chlorine and ClF_3O do not interact. An equimolar mixture (100 cm³, 4.46 mmol each) of the two when heated at 200° for 16 hr in a 30-ml stainless steel cylinder did result in complete consumption of the ClF_3O. The products were separated by fractional condensation at −142 and −196° and analyzed by infrared spectroscopy and gas chromatography. Chlorine monofluoride was the principal product (262 cm³, 11.7 mmol) with only a small amount of ClO_2F (6.7 cm³, 0.3 mmol) and unreacted Cl_2 (15.7 cm³, 0.7 mmol) being observed. Noncondensables (O_2) were also produced. When kept at 100° for 2 days, ClF_3O reacted with Cl_2 only partially (~30%) to give ClF_3, ClF, and ClO_2F as the major reaction products.

With Dichlorine Monoxide.—Chlorine trifluoride oxide (76.5 cm³, 3.42 mmol) and an equal quantity of Cl_2O were separately condensed at −196° into a Kel-F reactor fitted with a Teflon valve. (Previous experiments in stainless steel cylinders resulted in extensive decomposition of the Cl_2O, apparently due to

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[1] D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

[2] D. Pilipovich, R. H. H. Rogers, and D. Wilson, *ibid.*, **11**, 2192 (1972).

[3] K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2196 (1972).

[4] K. O. Christe, C. J. Schack, and D. Pilipovich, *ibid.*, **11**, 2205 (1972).

[5] V. H. Dayan and B. C. Neale, *Advan. Chem. Ser.*, **No. 54**, 223 (1966).

[6] C. J. Schack and B. C. Lindahl, *Inorg. Nucl. Chem. Lett.*, **3**, 387 (1967).

[7] C. J. Schack and R. D. Wilson, *Inorg. Chem.*, **9**, 311 (1970).

[8] E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. G. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

[9] G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **4**, 1497 (1965).

reaction with the fluorinated metal surface.) The reactor was allowed to warm slowly to ambient temperature. After a total reaction period of 15 hr, the sample was separated by fractional condensation at −95, −112, −142, and −196°. Unreacted Cl_2O and ClF_3O were recovered (134 cm^3, 5.98 mmol total), together with ClF (17.5 cm^3, 0.78 mmol) and ClO_2F (10.3 cm^3, 0.46 mmol).

With Chlorine Fluorosulfate.—Equimolar amounts (34.2 cm^3, 1.53 mmol) of ClF_3O and $ClOSO_2F$ were separately condensed into a prepassivated 10-ml stainless steel cylinder at −196°. The cylinder was allowed to warm to ambient temperature and to stand for 5 days. The reaction products were separated by several fractional condensations in a series of U traps cooled to −80, −95, −142, and −196°. Some unreacted ClF_3O was found, but all the $ClOSO_2F$ had been consumed. The materials formed were SO_2F_2 (13.0 cm^3, 0.58 mmol), $S_2O_5F_2$ (9.17 cm^3, 0.43 mmol), ClF (26.8 cm^3, 1.20 mmol), and ClO_2F (24.0 cm^3, 1.07 mmol).

With Tetrafluorohydrazine.—At ambient temperature, chlorine trifluoride oxide and N_2F_4 do not react. An equimolar mixture of the two (99.4 cm^3, 4.44 mmol each) was heated in a stainless steel cylinder at 130° for 65 hr before separating the products by fractional condensation. No unreacted N_2F_4 was recovered, but 45.7 cm^3 of ClF_3O (2.04 mmol) remained. The principal nitrogen containing product was NF_3 (120 cm^3, 5.35 mmol), some of which may have been lost by incomplete condensation in the trap cooled to −196°. Nitrosyl fluoride (62.6 cm^3, 2.80 mmol) and ClF (53.8 cm^3, 2.40 mmol) were also obtained along with trace amounts of FNO_2, NF_3O, and ClO_2F. At 100° for 24 hr, ClF_3O and N_2F_4 reacted in the same fashion but somewhat less than half the N_2F_4 was consumed.

Photolysis with Tetrafluorohydrazine.—Measured amounts of ClF_3O (85.6 cm^3, 3.82 mmol) and N_2F_4 (48.0 cm^3, 2.14 mmol) were condensed into a stainless steel cylinder cooled to −196°. The cylinder was equipped at its upper end with a uv grade sapphire window (5-in. diameter). After warming to ambient temperature, the contents of the cylinder was irradiated for 2 hr with a Hanovia utility lamp before separating the products. Multiple fractional condensations through U-traps cooled to −78, −95, −142, and −196° were used for this purpose. Considerable amounts of unreacted ClF_3O (60.2 cm^3, 2.69 mmol) were recovered, but all the N_2F_4 had been consumed. The products were NF_3 (68.5 cm^3, 3.06 mmol), FNO + FNO_2 (15.5 cm^3, 0.69 mmol), ClF (23.2 cm^3, 1.04 mmol), and ClF_3 (2.3 cm^3, 0.10 mmol) The chlorine trifluoride was isolated with an equivalent amount of FNO owing to the formation of the $NO^+ClF_4^-$ complex[10] in the trap cooled to −78°. The discrepancy in the nitrogen material balance for the reaction is ascribed to the incomplete condensation of NF_3 at −196° since no solid residues were observed in the reactor. Mixtures of ClF_3O and N_2F_4 were also irradiated in a cylinder with a 1-in. diameter sapphire window. In these experiments, very little reaction occurred even with prolonged irradiation (2 days) and approximately 90% of the reactants was recovered. The products were NF_3O, NF_3, FNO, ClF_3, and ClF.

With Difluoramine (*Caution!*)[11] **and Difluoraminocarbonyl Fluoride.**—A Kel-F reactor fitted with a Teflon valve was used to avoid the incompatibility problems of ClF_3O (and generated HF) with glass and HNF_2 with metal. From the glass line, HNF_2 (61.0 cm^3, 2.72 mmol) was loaded at −142°, and after attachment of the container to the metal line, ClF_3O (35.9 cm^3, 1.60 mmol) was condensed in at the same temperature. The closed reactor was warmed to −78° for 15 min before fractionation in the metal line was started through U traps cooled to −78, −95, −142, and −196°. The two warmest traps contained HF (not measured) and ClF_3O (8.1 cm^3, 0.36 mmol). The −142° fraction was an approximately equimolar mixture of ClO_2F and Cl_2 (total 6.2 cm^3, 0.28 mmol) with a trace of ClF_3. The −196° fraction consisted of NF_3O (19.5 cm^3, 0.87 mmol), NF_2Cl (19.4 cm^3, 0.87 mmol), and N_2F_4 (10.0 cm^3, 0.45 mmol). No unreacted HNF_2 was observed, although the N_2F_4 may have arisen in part from the decomposition of HNF_2 in the metal system during workup.

A similar reaction was observed between excess ClF_3O and NF_2CFO (46 cm^3, 2.05 mmol). However, in this case, the predominant N–F product was N_2F_4 (18 cm^3, 0.8 mmol) and COF_2 (46 cm^3, 2.05 mmol), with much less NF_3O and NF_2Cl (~5 cm^3 each).

With Platinum Hexafluoride.—Platinum hexafluoride (32.2 cm^3, 1.44 mmol) and ClF_3O (48.4 cm^3, 2.16 mmol) were combined at −196° in a prepassivated 10-ml Monel cylinder. The contents of the cylinder was allowed to warm up slowly to room temperature and was kept at this temperature for 15 hr. Subsequently, the cylinder was cooled to −196° and 14.8 cm^3 (0.66 mmol) of material volatile at −196° was removed. The volatile material was identified as F_2 by its vapor pressure at −196° and mass spectrum. The contents of the cylinder was allowed to warm to ambient temperature, and 14.8 cm^3 (0.66 mmol) of volatile material was removed at this temperature which consisted, according to its infrared spectrum, of ClF_3O. The cylinder was opened in the glove box and contained 0.57 g of a bright yellow solid, which was identified by vibrational spectroscopy as $ClF_2O^+PtF_6^-$. Therefore, PtF_6 (1.44 mmol) had reacted with ClF_3O (1.50 mmol) in a mole ratio of 1:1.04, producing F_2 (0.66 mmol) and the solid complex, $ClF_2O^+PtF_6^-$.

Results and Discussion

Chlorine trifluoride oxide reacts with numerous materials causing oxidation through both fluorination and oxygenation. With hydrogen-containing species, these reactions may occur at quite low temperature and with hydrocarbon-type compounds are generally explosive. However, many chlorine, fluorine, or oxygen substituted compounds, even with lower valent central atoms, react only slowly at ambient temperature, or not at all. Thus, no reaction was observed at room temperature between ClF_3O and chlorine, chlorine fluorides, chlorine oxyfluorides, and the nitrogen fluorides, FNO, FNO_2, NF_3, and N_2F_4. However, elevated temperatures or uv photolysis have resulted in appreciable reaction of all compounds examined.

Reactions of chlorine and ClF_3O were carried out as a means of assessing the possible courses by which the oxyfluoride might undergo reduction. Basically, this could occur through fluorination or oxygenation of the Cl_2 starting material. A controllable fluorination reaction would be particularly desirable since it might yield the unknown compound, FClO. Whereas at 25°, no interaction was detected, at 200° the following reaction occurred

$$ClF_3O + Cl_2 \longrightarrow 3ClF + 0.5O_2$$

It is tempting to interpret this equation in terms of direct oxygen elimination from ClF_3O, followed by equilibration[12] of ClF_3 and Cl_2 to ClF. However, the following evidence suggests the participation of chlorine in the initial reduction step: (1) ClF_3O alone does not undergo substantial thermal degradation under these conditions;[1] and (2) experiments at lower temperature showed ClF_3, ClF, and ClO_2F as major reaction products. These results might be rationalized by assuming the following reaction sequence involving FClO as an unstable intermediate.

$$\begin{array}{l} 2ClF_3O + 2Cl_2 \longrightarrow 2[FClO] + 4ClF \\ 2[FClO] \longrightarrow ClO_2F + ClF \\ ClO_2F \longrightarrow ClF + O_2 \\ \hline 2ClF_3O + 2Cl_2 \longrightarrow 6ClF + O_2 \end{array}$$

The thermal decomposition of ClO_2F in quartz to ClF

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[10] E. D. Whitney, R. O. MacLaren, T. J. Hurley, and C. E. Fogle, *J. Amer. Chem. Soc.*, **86**, 4340 (1964).

[11] *Caution!* Difluoramine should not be cooled below −142° because of its pronounced tendency to explode after being in the solid state. In addition, chlorine fluorides or oxyfluorides must be free from chlorine oxide impurities for reactions with difluoramine since such impurities often cause explosive deflagration.

[12] H. Schmitz and H. J. Schumacher, *Z. Naturforsch. A*, **2**, 359 (1947).

and O_2 has previously[13] been demonstrated. The fact that this reaction appears to proceed in our experiments at lower temperature might be explained by the catalytic influence[14] of metal fluorides. As an alternative, the decomposition of the unstable FClO may vary with reaction temperature. Thus, at lower temperature, FClO might decompose to ClO_2F and ClF, whereas at higher temperature it might yield directly ClF and O_2. The assumption of an unstable FClO intermediate is reasonable. Numerous chlorine fluoride reaction systems, such as ClF_3–H_2O,[14] ClF_3–$HONO_2$,[15] or ClF_3O–Cl_2O (see below), are best interpreted by assuming the formation of an unstable FClO intermediate. In addition, our repeated efforts to synthesize and isolate a stable FClO moiety[15] have been unsuccessful.

Chlorine monoxide and ClF_3O reacted slowly at room temperature. The use of an inert material for the reactor (Kel-F) allowed the course of the reaction to be determined without extensive, interfering side reactions.

$$ClF_3O + Cl_2O \longrightarrow 2ClF + ClO_2F$$

Again, the fluorination of a chlorine atom (of Cl_2O) appears to be a plausible first reaction step, followed by the formation and decomposition of an unstable FClO intermediate (see above). This reaction of Cl_2O and ClF_3O may also account, at least in part, for the less than theoretical yields of ClF_3O in its synthesis from Cl_2O.[1]

Chlorine fluorosulfate and ClF_3O reacted at ambient temperature forming the products described by the following equations

$$ClF_3O + 2ClOSO_2F \longrightarrow S_2O_5F_2 + ClO_2F + ClF$$
$$ClF_3O + ClOSO_2F \longrightarrow SO_2F_2 + ClO_2F + ClF$$

which account for 60 and 40%, respectively, of the $ClOSO_2F$ consumed. The formation of $S_2O_5F_2$ obviously involves a complex process, including at some point the abstraction of oxygen from the SO_3F group. Indeed, the failure to find either $S_2O_6F_2$ or SO_3F_2 as products suggests that SO_3F radicals are not involved in the reaction. Further, it appears that the overall process may be quite similar to that noted[1] in the preparation of ClF_3O from Cl–O–X species (where X is any other radical, such as Cl, NO_2, or SO_2F). Namely, fluorination of the chlorine atom of the hypochlorite group facilitates O–X bond rupture in preference to the Cl–O bond-breaking process. Such a mechanism would yield SO_2F radicals which can either be fluorinated to SO_2F_2 or can react with additional $ClOSO_2F$ to give $S_2O_5F_2$. However, direct fluorination at the sulfur of $ClOSO_2F$ cannot be excluded as an alternate route to SO_2F_2. The chlorine compounds produced, ClF and ClO_2F, are again the same as those generally obtained from ClF_3O on reaction with Cl–O-containing compounds as expected for an unstable FClO intermediate.

Tetrafluorohydrazine and ClF_3O reacted at an appreciable rate only above 100°. Nitrogen trifluoride and nitrosyl fluoride were obtained in fair agreement with the stoichiometry shown.

$$ClF_3O + 2N_2F_4 \longrightarrow 3NF_3 + FNO + ClF$$

The nitrogen fluoride products are the result of oxygenation and fluorination by ClF_3O. Overall, the reaction is quite similar to that reported[16] for N_2F_4 and OF_2 which also yielded NF_3 and FNO in a 3:1 ratio. Only a trace of the more highly oxidized nitrogen fluoride, NF_3O, was observed. However, this indicated that alternate conditions might more fully take advantage of the ability of ClF_3O to fluorinate and oxygenate. To this end, ultraviolet irradiations of N_2F_4–ClF_3O mixtures were carried out. It was found that limitation of the intensity of the uv irradiation (through the use of a small reactor window, 1-in. diam) allowed greater amounts of NF_3O to be formed than in the thermal reaction. But these quantities were still small, about 5 mol %/mol of N_2F_4. Increasing the window area (and hence the admitted light) by a large factor led to complete conversion of the N_2F_4 to NF_3, FNO, and FNO_2. No attempts were made to maximize conditions for oxidizing N_2F_4 to NF_3O using ClF_3O.

Chlorine trifluoride oxide and difluoramine underwent smooth, fast reaction at temperatures where pure ClF_3O is a solid. Three N–F-containing compounds, NF_3O, $ClNF_2$, and N_2F_4, were formed and the first two of these were always produced in nearly equimolar amounts. Thus, the major reactions may be

$$\begin{array}{l} ClF_3O + 2HNF_2 \longrightarrow [FClO] + 2HF + 2NF_2\cdot \\ 2NF_2\cdot + [FClO] \longrightarrow NF_2Cl + NF_3O \\ \hline ClF_3O + 2HNF_2 \longrightarrow NF_2Cl + NF_3O + 2HF \end{array}$$

accompanied by the following competing reactions

$$\begin{array}{l} 2NF_2\cdot \longrightarrow N_2F_4 \\ 2[FClO] \longrightarrow ClO_2F + ClF \\ ClF + HNF_2 \longrightarrow HF + NF_2Cl \\ \hline 2[FClO] + HNF_2 \longrightarrow ClO_2F + NF_2Cl + HF \end{array}$$

The high yield of NF_3O (70% based on ClF_3O consumed) noted here is remarkable when compared to previously reported[17,18] and unreported[19,20] yields obtained under a variety of conditions.

The reaction between difluoraminocarbonyl fluoride, F_2NCFO, and ClF_3O yielded again NF_3O and $ClNF_2$ in nearly equimolar amounts. However, the yields were much lower (20% based on ClF_3O consumed) with N_2F_4 being the main N–F containing product. By analogy with the HNF_2–ClF_3O reaction (see above), the following reaction sequence might be proposed

$$\begin{array}{l} ClF_3O + 2F_2NCFO \longrightarrow 2COF_2 + [FClO] + 2NF_2\cdot \\ 2NF_2\cdot + [FClO] \longrightarrow NF_2Cl + NF_3O \\ \hline ClF_3O + 2F_2NCFO \longrightarrow NF_2Cl + NF_3O + 2COF_2 \end{array}$$

with the competing reactions being identical with those written for the ClF_3O–HNF_2 reaction.

The formation of the ClF_2O^+ cation by the reaction

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[13] M. J. Heras, P. J. Aymonino, and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, **22**, 161 (1959).

[14] R. Bougon, M. Carles, and J. Aubert, *C. R. Acad. Sci., Ser. C*, **265**, 179 (1967).

[15] K. O. Christe, *Inorg. Chem.*, **11**, 1220 (1972).

[16] M. Rubinstein, J. E. Sicre, and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, **43**, 51 (1964).

[17] (a) N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966); (b) N. Bartlett and S. P. Beaton, *ibid.*, 167 (1966); (c) N. Bartlett, S. P. Beaton, and N. K. Jha, *ibid.*, 168 (1966).

[18] W. B. Fox, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2604 (1966).

[19] E. A. Lawton and D. Pilipovich, U. S. Patent 3,505,015 (April 7, 1970); British Patent 1,104,711 (Feb 15, 1965).

[20] Just as Bartlett and coworkers showed that PtF_6 or OsF_6 reacts with FNO to give low or trace amounts of NF_3O, so also ClF_5 and FNO have been noted to form slight amounts of NF_3O: D. Pilipovich and H. F. Bauer, unpublished results.

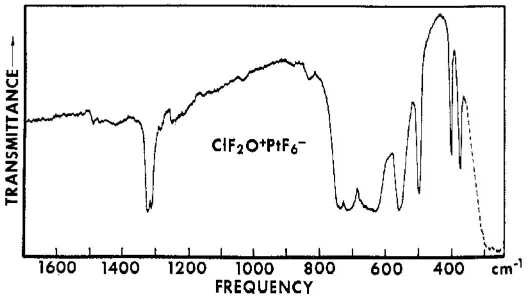

Figure 1.—Infrared spectrum of solid $ClF_2O^+PtF_6^-$ as AgCl disk.

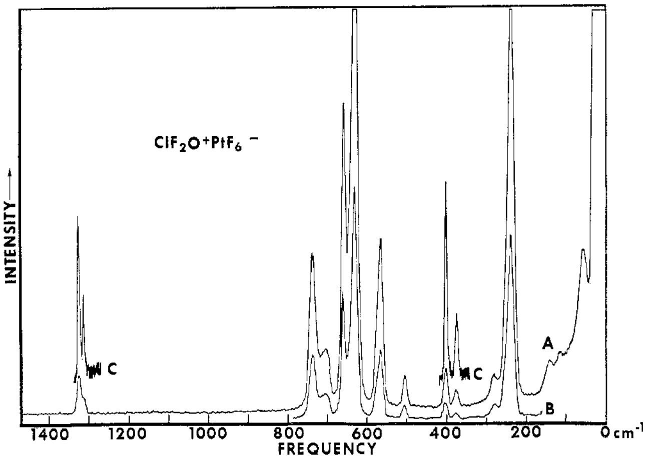

Figure 2.—Raman spectrum of solid $ClF_2O^+PtF_6^-$ at three different recorder voltages: exciting line 6471 Å; spectral slit width for curves A and B 8 cm⁻¹; for curve C 2 cm⁻¹.

of ClF_3O with strong Lewis acids is reported elsewhere.[4,21] The same cation was found to result from the interaction of platinum hexafluoride and ClF_3O, according to

$$ClF_3O + PtF_6 \longrightarrow ClF_2O^+PtF_6^- + 0.5F_2$$

While all the reactions described earlier in this report showed ClF_3O functioning as an oxidizing agent, here it can be seen that platinum hexafluoride is the more powerful oxidizing agent. However, the oxidation is confined to one of the fluorine ligands of ClF_3O and does not affect the oxidation state of the chlorine central atom which would result in the most interesting ClF_5O molecule. All the PtF_6 reacted and excess ClF_3O was recovered unchanged.

The bright yellow, crystalline solid, $ClF_2O^+PtF_6^-$, was characterized by vibrational spectroscopy. Figures 1 and 2 show the infrared and Raman spectrum, respectively, of the solid. Table I lists the observed frequencies together with their assignment. All bands expected for ClF_2O^+ [21] have been observed with proper frequencies and intensities. In addition to the ClF_2O^+ bands, the vibrational spectrum shows the bands characteristic[22] for PtF_6^-. Consequently, the solid obtained from the ClF_3O–PtF_6 reaction has the ionic composition $ClF_2O^+PtF_6^-$.

The X-ray powder diffraction pattern of $ClF_2O^+PtF_6^-$ is listed in Table II. The observed lines were indexed on the basis of an orthorhombic unit cell with $a = 9.94$, $b = 11.12$, and $c = 8.21$ Å. Assuming that the volume of the oxygen atoms will be comparable to that of the fluorine atoms, and neglecting contributions from the highly charged central atoms to the volume (as suggested by Zachariasen[23,24]), an average volume of 17–18 Å³ can be expected for each fluorine or oxygen atom in $ClF_2O^+PtF_6^-$. Thus, values of 17.8 and 17.0 Å³ have been reported for $IF_6^+AsF_6^-$ [25] and $NF_4^+AsF_6^-$,[26] respectively. Based on this assumption, one can deduce six molecules per unit cell for $ClF_2O^+PtF_6^-$, resulting in an average volume of 16.81 Å³ per F or O atom. The powder pattern of $ClF_2O^+PtF_6^-$ is similar

Table I

Vibrational Spectrum of $ClF_2O^+PtF_6^-$ and Its Assignment Compared to That of $ClF_2O^+AsF_6^-$ [a]

Observed frequency, cm⁻¹				Assignment (for ClF_2O^+ in C_s)
$ClF_2O^+PtF_6^-$		$ClF_2O^+AsF_6^-$		
Ir	Raman	Ir	Raman	
1326 ms	1324 (0.6)[b]	1331 ms	1333 (2)[b]	$\nu_1(A')$ ^{35}Cl
1313 mw	1311 (0.2)	1319 mw	1320 (1)	$\nu_1(A')$ ^{37}Cl
737 s	737 (2.7)	750 br, s	757 br (3)	$\nu_2(A')$
705 s	705 (0.8)	695 vs	696 (1)	$\nu_5(A'')$
643 vs	658 (4.2)	695 vs		XF_6^-
630 sh	630 (10)	675 sh, w	674 (10)	
	575 sh			
564 s	564 (2.9)	561 ms	563 (3)	
508 s	506 (0.5)	509 ms	511 (2)	$\nu_3(A')$
401 ms	401 (0.7)	407 s	406 (2)	$\nu_6(A'')$
		388 s		XF_6^-
386 ms	386 (0.2)	378 sh	378 sh	$\nu_4(A')$
	280 (0.3)		371 (4)	XF_6^-
	239 (7.9)			Lattice modes
	140 (0.3)			
	115 (0.2)			
	58 (1.0)			

[a] K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, 11, 2212 (1972). [b] Uncorrected Raman intensities.

Table II

X-Ray Powder Data for $ClF_2O^+PtF_6^-$

d, Å			
Obsd	Calcd	Intensity	*hkl*
7.43	7.43	mw	110
5.47	5.50	m	111
4.95	4.97	mw	200
4.25	4.26	vs	201
4.09	4.10	s	002
3.72	3.70	ms	030
3.61	3.60	vw	112
3.38	3.37	w	031
3.31	3.31	s	300
3.17	3.17	m	310
3.02	3.04	w	212
2.98	2.99	ms	231
2.86	2.85	w	320
2.77	2.78	m	040
2.59	2.57	m	302
2.48	2.49	m	400
2.33	2.34	mw	322
2.20	2.20	ms	223
2.14	2.15	vw	051
2.07	2.07	vw	313
2.04	2.03	m	250
1.99	1.99	mw	500
1.93	1.93	ms	501

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(21) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, **11**, 2212 (1972).

(22) N. Bartlett, *Angew. Chem., Int. Ed. Engl.*, **7**, 433 (1968); N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966).

(23) W. H. Zachariasen, *J. Amer. Chem. Soc.*, **70**, 2147 (1948).

(24) F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).

(25) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 1783 (1967).

(26) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966).

to that observed[27] for $ClO_2^+AsF_6^-$. The latter has a tetragonal unit cell with a = 10.39 and c = 8.03 Å. The unit cell of $ClF_2O^+PtF_6^-$ might be derived from the $ClO_2^+AsF_6^-$ cell by assuming orthorhombic distortion due to the lower symmetry of the ClF_2O^+ cation. Further evidence for the formulation of the solid as $ClF_2O^+PtF_6^-$ can be deduced from the fact that the X-ray powder diffraction patterns of $ClF_2O^+AsF_6^-$ [4] and $ClF_2O^+PtF_6^-$ are almost identical.

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[27] K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

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Chlorine Trifluoride Oxide. V. Complex Formation with Lewis Acids and Bases

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Chlorine trifluoride oxide, ClF_3O, exhibits amphoteric character. With the strong Lewis bases CsF, RbF, and KF it forms the stable, white, crystalline adducts, $CsF\cdot ClF_3O$, $RbF\cdot ClF_3O$, and $KF\cdot ClF_3O$, respectively. With the weaker base FNO it neither forms a complex nor chemically interacts at temperatures as low as −95°. With the Lewis acids SbF_5, AsF_5, and BF_3 it forms white, crystalline 1:1 adducts, whereas with SiF_4 it forms a 2:1 adduct. The thermal stability of these adducts decreases in the order: $ClF_3O\cdot SbF_5 > ClF_3O\cdot AsF_5 > ClF_3O\cdot BF_3 > (ClF_3O)_2\cdot SiF_4$. The dissociation pressure–temperature relation has been measured and thermodynamic data are calculated for the process $(ClF_3O)_2\cdot SiF_4(s) \rightleftharpoons 2ClF_3O(g) + SiF_4(g)$. The tendencies of adduct formation are compared for ClF_3O, ClF_5, ClO_2F, ClF_3, and ClF and are correlated with the structural stability of the halogen fluorides and their corresponding ions.

Introduction

Halogen fluorides and oxyfluorides generally exhibit amphoteric character.[1] Consequently, we considered that ClF_3O might also form complexes with strong Lewis acids and bases. In this paper we report on the syntheses and some of the properties of a number of adducts derived from ClF_3O.

Experimental Section

Materials and Apparatus.—Experimental techniques used in these studies were essentially the same as those described elsewhere.[2-6] The preparation and purification of ClF_3O and FNO are described elswhere.[2,7] The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. Arsenic pentafluoride (from Ozark Mahoning Co.), BF_3, and SiF_4 (both from the Matheson Co.) were purified by fractional condensation. Antimony pentafluoride (from Ozark Mahoning Co.) was purified by vacuum distillation at ambient temperature. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

Preparation of Alkali Metal Fluoride–ClF_3O Adducts.—Dry CsF (66.0 mmol) was placed into a 90-ml prepassivated Monel cylinder, and purified ClF_3O (106.4 mmol) was added at −196°. The cylinder was kept at ambient temperature for 30 days. Unreacted ClF_3O (40.5 mmol) was removed *in vacuo* and identified by its infrared spectrum. The cylinder was opened in the glove box and contained 17.1 g of a stable, white, crystalline solid (weight calculated for $Cs^+ClF_4O^-$, 17.18 g). Therefore, CsF (66.0 mmol) had reacted with ClF_3O (65.9 mmol) in a mole ratio of 1:0.998 producing the complex $Cs^+ClF_4O^-$.

Similarly, RbF (92.0 mmol), when combined with ClF_3O (93.5 mmol) at −196° and shaken at ambient temperature for 2 days, reacted with ClF_3O (67.15 mmol) producing the complex $Rb^+ClF_4O^-\cdot 0.28RbF$.

Pure ClF_3O (purity 99+%) was loaded into a 316 stainless steel cylinder containing a large excess of dry KF. After the contents of the cylinder was kept at ambient temperature for 30 days, practically all of the ClF_3O had complexed with KF.

The FNO–ClF_3O System.—Nitrosyl fluoride (25.6 mmol) and ClF_3O (12.8 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm to −79° and was kept at this temperature for 24 hr. It remained at all times a water-clear liquid and no sign of solid formation could be observed. The vapor pressure above the liquid was about 115 mm. The contents of the trap was cooled to −95°, and FNO (25.5 mmol) was removed by vacuum distillation. The residue (12.7 mmol) was shown by its infrared spectrum to be essentially pure ClF_3O. Hence, ClF_3O and FNO do not form a stable complex at −95°.

Preparation of $ClF_3O\cdot$Lewis Acid Adducts.—Boron trifluoride (4.00 mmol) and ClF_3O (3.22 mmol) were combined at −196° in a Teflon FEP container. The mixture was allowed to warm up slowly to ambient temperature and was kept at this temperature for 12 hr. Unreacted BF_3 (0.74 mmol) was removed *in vacuo* at 20° and identified by its infrared spectrum. The white, crystalline residue had no detectable dissociation pressure at 20°. Therefore, ClF_3O (3.22 mmol) had reacted with BF_3 (3.26 mmol) in a mole ratio of 1:1.01, producing the complex $ClF_3O\cdot BF_3$.

Similarly, AsF_5 (16.4 mmol) and ClF_3O (13.2 mmol) were combined at −196°. After keeping the mixture at 20° for 2 hr, unreacted AsF_5 (2.8 mmol) was removed *in vacuo* at 20°. Therefore, ClF_3O (13.2 mmol) had reacted with AsF_5 (13.6 mmol) in a mole ratio of 1:1.03 producing the white, crystalline, stable complex, $ClF_3O\cdot AsF_5$.

Silicon tetrafluoride (3.79 mmol) was combined with ClF_3O (5.02 mmol) at −196°. When the mixture was allowed to warm up to about −80°, complex formation occurred. Unreacted SiF_4 (1.21 mmol) was removed *in vacuo* at −64° and identified by its infrared spectrum. Therefore, ClF_3O (5.02 mmol) had reacted with SiF_4 (2.58 mmol) in a mole ratio of 2:1.03, producing the white, crystalline complex $(ClF_3O)_2\cdot SiF_4$.

Antimony pentafluoride (104 mmol) and ClF_3O (20.9 mmol) were combined in a 150-ml prepassivated Monel cylinder at −196°. The contents of the cylinder was kept in an electrically heated oven at 135° for 6 days under autogenous pressure. Unreacted SbF_5 was removed by vacuum distillation at 130°.

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[1] L. Stein in "Halogen Chemistry," Vol. 1, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, Chapter 3.

[2] D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

[3] D. Pilipovich, H. H. Rogers, and R. D. Wilson, *ibid.*, **11**, 2192 (1972).

[4] K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2196 (1972).

[5] C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *ibid.*, **11**, 2201 (1972).

[6] D. Pilipovich, R. D. Wilson, and H. F. Bauer, U. S. Patent, to be issued, 1972.

[7] K. O. Christe, *Inorg. Chem.*, **11**, 1220 (1972).